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## Tuning of Reversible Thermochromic Properties of Salicylaldehyde Schiff bases through the substitution of Methoxy and Nitro Groups

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#### Abstract

In this study, in order to explore the new kinds of reversible thermochromic materials, four salicylaldehyde Schiff bases (BSP1-4) substituted with methoxy and nitro groups were synthesized and their reversible thermochromic properties were investigated. All compounds were characterized by HNMR, IR, UV-vis, TG-DSC, and SEM techniques. Through HNMR, IR and UV-vis spectra, four target products display different colors. The UV-Vis spectra show that the type and position of the substituents of BSPs can control the absorption wavelength by changing the electronic transition mode, which leads to the difference of the color of the samples. With the increase of light colored samples, the content of the  $\Delta E1$  gradually increases until the maximum value of 48.6. TG-DSC result indicates good thermal stability of the BSP below 350 °C. SEM images show that the surface morphologies of four BSP samples are different, including flake, rod and strip. The thermochromic properties of the BSP samples were evaluated using variable temperature FT-IR spectroscopic, solid UV-Vis spectra and response time. DFT calculations were conducted to rationalize the optical behavior of the BSP samples in Enol and Ketone form. The results of

variable temperature FT-IR support the hypothesis that the reversible thermochromic mechanism of salicylaldehyde Schiff base is proton transfer. Among all of BSPs, the BSP1 has the best reversible thermochromic cycle stability ( $\Delta$ E2=2.6) and the shortest response time (10s) which can be used as the new promising thermochromism materials.

*Keywords*: Salicylaldehyde Schiff base, reversible thermochromism, cycle stability, response time

#### 1. Introduction

In recent years, thermochromic materials have attracted wide attention due to their potential applications in industrial, medical, military and other fields <sup>[1-2]</sup>. They are commonly used as temperature monitoring materials in the industrial field <sup>[3]</sup>. It can be used not only as a temperature indicator coating to monitor the temperature of the instrument <sup>[4]</sup>, but also as a building coating to provide cool hue in summer and warm tone in winter, thus reducing the energy consumption of the building environment in any season <sup>[5-6]</sup>. Beside these, they can also be used as a temperature measurement material in the medical field <sup>[7]</sup>, for example, the clinical thermometer material and the indication of temperature changes during the treatment. It is also reported that the polydiacetylene microcapsule biosensor with a thermochromic effect can recognize small molecules by the color change caused by heating, and has a strong response <sup>[8-9]</sup>. At the same time, the coating of thermochromic material can be used as the coating in military technology to change the color of military equipment to match the surrounding environment, thus reducing the probability of detection <sup>[10]</sup>. Current

findings show that the synthesis of thermochromic materials is mainly concentrated on inorganic materials such as VO<sub>2</sub> <sup>[11]</sup> and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> <sup>[12]</sup>. However, VO<sub>2</sub> and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> are not only expensive and dangerous, but also have high discoloration temperature. In addition, our group has studied the inorganic thermochromic materials of ZnO doped by different density Co for visible light stealth <sup>[13]</sup>. It is found that the ZnO thermochromic materials<sup>[14]</sup> also encounter with the problems of high discoloration temperature and long response time to heat. Therefore, the applications of inorganic thermochromic materials has been greatly limited in the low-temperature area.

Currently, organic thermochromic materials<sup>[15]</sup> have aroused widespread concern because of their low discoloration temperature, short response time and variable colors characteristics as compared to the inorganic thermochromic materials <sup>[16]</sup>. Spirocyclic compounds, triphenylmethanes, fluorocarbons and Schiff bases are the widely studied organic thermochromic materials <sup>[17-19]</sup>. Among them, because of its ease of synthesis, great varieties in the discoloration temperatures with different structures <sup>[20-21]</sup>, and excellent performance in many fields, Schiff bases have been attracted more and more attention in the thermochromic material area <sup>[22-23]</sup>. At present, the Schiff bases have been widely reported in biomedical, metal complexes <sup>[24-27]</sup> and military applications<sup>[28]</sup>. Because Schiff bases can be used as a ligand to combine with various metal ions, the scope of research in the biomedicine field has been expanded<sup>[29]</sup>. For example, the combination of Schiff base with specific metal ions can achieve molecular recognition <sup>[30-33]</sup>, and Schiff base metal complexes can

also act as catalysts to catalyze cell viability<sup>[34-35]</sup>. Since from the eighties of last century, the thermochromic and photochromic properties of Schiff base<sup>[36]</sup> have been extensively studied and many studies have shown that the thermochromic mechanism of salicylaldehyde Schiff base is proton transfer<sup>[37-38]</sup>. The research on the salicylaldehyde Schiff base thermochromic effect is also expected to contribute to the development of new thermochromism materials based on the rich color and good thermochromism properties of Schiff base.

In this work, four salicylaldehyde Schiff bases (BSPs) with different substituents were synthesized and characterized as demonstrated in Fig. 1. The color of the product can be effectively controlled by changing the absorption wavelength through shifting the position of the substituent. Through the regulation of precursors, the energy band regulation of Schiff base is realized, and the mechanism of thermochromism is effectively revealed. At the same time, the structure and color of BSPs, the reversible thermochromic mechanism and the properties of BSPs were systematically studied.

#### 2. Experimental

#### 2.1. Materials

The ethanol and N-N'-dimethylformamide (DMF) were purchased from Nanjing Chemical Reagent Co., Ltd. and were used as received without further purification. P-phenylenediamine, Salicylaldehyde (AR, 98% purity), 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde and 5-nitrosalicylaldehyde (98% purity) were purchased from Aladdin.

#### 2.2 Methods

#### 2.2.1 Synthesis of N, N'- Bis (salicylidene) -p-phenylenediamine (BSP1)

Synthesis of BSP1 was carried out by refluxing p-phenylenediamine and salicylaldehyde in ethanol according to the method previously reported<sup>[27]</sup>. 10ml ethanol solution of 1mmol (0.108g) p-phenylenediamine was stirred for 1h at 40 °C. 2 mmol(0.244g) salicylaldehyde was dissolved in 40 ml ethanol and was slowly added to the reaction mixture at 40 °C and heated at 70 °C for 4 hours. After the completion of the reaction, the precipitate was washed three times with a large amount of ethanol, and then the product was recrystallized with DMF. The solid was dried at 80 °C for 24h in a vacuum oven and the resulting product was carefully collected which was the orange-yellow solid crystallographic sample and the yield rate is around 80.0 %.

2.2.2 Synthesis of N,N'-Bis(3-methoxysalicylidene)-p-phenylenediamine (BSP2) and N,N'-Bis(4-methoxysalicylidene)-p-phenylenediamine (BSP3)

The N,N'-Bis(3-methoxysalicylidene)-p-phenylenediamine (BSP2) and N,N'-Bis(4-methoxysalicylidene)-p-phenylenediamine(BSP3) were synthesized according to the methods reported in the literature<sup>[28]</sup>. The desired 2mmol(0.304g) 3-methoxysalicylaldehyde dissolved in 20 mL ethanol and the resulting mixture was then stirred for 1h at 40 °C. 1mmol(0.108g) p-phenylenediamine was dissolved in 30 ml ethanol and was slowly added to the reaction mixture at 40 °C. Then mixture was heated at 65 °C for 4 hours. The reaction mixture was washed repeatedly with ethanol and recrystallized from DMF. The resulting product was an orange-red powder sample, and the yield rate was around 81.0 %.

The BSP3 was then prepared in the same way as BSP2. The prepared product was the lemon yellow crystalline solid and the yield rate was around 83.0%.

#### 2.2.3 Synthesis of N,N'-Bis(5-nitrosalicylidene) -p-phenylenediamine (BSP4)

The crude product was obtained by the above method using a similar route applied for BSP2 and BSP3<sup>[27, 29]</sup>. The reaction mixture was washed repeatedly with ethanol and recrystallized from DMF. The product was deep yellow powder sample, and the yield rate was around 78.0%.

## 2.3 Characterization of Salicylaldehyde Schiff Base (BSPs)

The 1HNMR were acquired using a spectrometer Bruker AvanceIII-400, operating at 400 MHz. For the analyses, the samples were dissolved in CDCl<sub>3</sub> at a concentration of 10 mg /mL. Infrared absorption spectra were obtained with a Nexus 670 FTIR spectrometer operated in the range 4000-500 cm<sup>-1</sup>. To get more information about the structures of the BSP1-4 at different temperatures, variable temperature infrared absorption spectra were carried out using an IR/Nicolet 6700 in the range 4000–500 cm<sup>-1</sup>, with a heating rate of 20 °C/min. Variable temperature infrared measurements for these four compounds were performed at 150 °C, 155 °C, 180 °C and 145 °C, respectively. The samples were prepared in the form of pellets with KBr (sample/KBr = 1% w/w), and a pure KBr disk was used as a reference. Electronic absorption spectral analysis was carried out using a Shimadzu 2450 UV-Vis spectrophotometer and the investigated wavelength were ranged from 200 to 800 nm. The 200-600 nm spectra were obtained using four liquid samples of a same concentration with DMF as a solvent. The 400-700 nm visible spectrum were obtained using four solid samples

previously dried in an oven at 80 °C. Approximately 2 mg of each samples were dispersed in 20 mg of barium sulfate. Calorimetry (TG-DSC) analysis was measured by a Mettler Toledo TGA Analyzer (SDTA851, Switzerland) from 25 to 500 °C in  $N_2$  at a heating rate of 10 °C/ min. The morphology was observed by a Carl Zeiss SIGMA scanning electron microscope with the accelerating voltage of 15 kV at liquid nitrogen atmosphere.

#### 2.4 Reversible thermochromic properties

The cover glasses ( $20 \times 20$ mm) were prepared with cleaning by ethanol. Four samples of equal amount (10mg) on the cover glasses were placed on the heating platform (FD-7000, 0-450 °C), and were numbered 1, 2, 3, 4 respectively. After that, the platform was heated up from room temperature to its corresponding decomposition temperature. The discoloration process of four samples were observed and recorded when four samples were removed from the heating platform and cooled to room temperature. The chromatic aberration ( $\Delta E1$ ) between the original samples and the samples after the thermochromism was measured by a Colorimeter (X-Rite). The operation( heating and cooling) was repeated to record chromatic aberration ( $\Delta E2$ ) between the color of samples at room temperature after 50 heating-cooling cycles and the original color of the samples. The reversible thermochromism cycle stability can be evaluated by comparing the chromatic aberration ( $\Delta E2$ . The response time includes heating discoloration time of the samples and cooling color reversible

time of the sample. This process uses a stopwatch to record the time which refers to the time from beginning discoloration to color stabilization and the color to be reversible when cooled.

#### 3. Results and discussion

#### 3.1 1HNMR spectroscopy

Table 1 shows a simplified table of the 1HNMR spectra of BSPs. The BSPs show clear chemical structure with exact assignments of hydrogen atoms from table 1. The chemical shift of 1H in different positions of the sample molecules are shown in the table 1. From table 1, the chemical shift of hydrogen (C-7) with about 8.57 to 9.10 ppm can be observed for the BSP1, BSP2, BSP3, and BSP4 samples, which were belong to -CH=N- in the products. The location of the hydroxyl group on the benzene ring is at about 13 ppm and the methoxy H in BSP2 and BSP3 appears between 3.8-3.9 ppm. In combination with the positions and area of H, the molecular structures of BSPs(1-4) have been determined.

#### 3.2 Infrared spectroscopy

Fig. 2 presents IR spectroscopy of BSPs. It is obvious that IR spectroscopy show almost identical peaks at 1610-1630 cm<sup>-1</sup>, demonstrating the similar chemical structures with BSPs. The main difference between BSPs and precursors is the newly formed imine structure (C=N) . In contrast to the precursor, the peaks at 1610-1630 cm<sup>-1</sup> of the products is the newly formed imine structure, which is not contained in the precursor. The characteristic peaks at 1622, 1615, 1613 and 1625cm<sup>-1</sup> are attributed to the stretching vibration of the imine structure(C=N) in the BSPs<sup>[30]</sup>. The broad peaks at around 3300cm<sup>-1</sup> is the absorption peak generated by the associative hydroxyl group in the BSPs. In addition, the peaks at 1305 and 1250 cm<sup>-1</sup> come from C-O-C

stretching in BSP2 and BSP3. With the conjugation with benzene ring,  $-NO_2$  symmetry and asymmetric stretching occurs at 1385 and 1522 cm-1, while C-N stretching occurs at 835 cm-1 for BSP 4.

#### 3.3 Electronic absorption spectra

All BSPs molecules have the same molecular skeleton with different substituents located on the phenolic ring. The electron absorption spectra of the BSP1, BSP2, BSP3 and BSP4 in the 200-800nm are shown in Fig.3(a-b). Although no substituents are connected to the phenolic structures of the BSP1 molecules, there are -OCH<sub>3</sub> and -NO<sub>2</sub> substituents in BSP2, BSP3 and BSP4 at different positions (ortho, meta, or para-positions) of the phenolic structures. Therefore, the spectral properties and molecular structure are affected by these substituents. As shown in Fig.3(a), BSP1 has a strong absorption peak in the 270-300 nm, which is caused by the n- $\pi$ \* electron transition of the imine group (-CH=N-) in the conjugated system. The absorption peak of benzene ring appears in the 230-250 nm. However, the -OCH<sub>3</sub> and -NO<sub>2</sub> of BSP2, BSP3 and BSP4 are connected to the benzene ring in the form of auxiliary chromium or chromophore, and change the energy level state of the  $\pi$  orbits. So, the absorption peaks of BSP2, BSP3 and BSP4 conjugated chains occurred red shift, corresponding to the strong absorption peak of 300-400 nm in Fig.3 (a).

Fig.3 (b) presents the visible spectrum of BSP's compounds. It can be seen that the peaks of BSP1, BSP2, BSP3 and BSP4 in the visible region appear in 400-550 nm. According to the theory of complementary colors<sup>[15]</sup>, the material absorbs light of a

certain color, and the material will display the complementary color of the certain color. Combining the actual colors of BSPs, the products absorb blue-green light in 400-500 nm, which in turn show complementary color yellow to orange range. In addition, due to the introduction of substituents, the UV-Vis absorption spectrum of BSPs move towards the long wavelength, and its yellowness tends to decrease (BSP3>BSP1>BSP4>BSP2).

#### 3.4 Thermal analysis

Thermogravimetric-Differential Scanning Calorimetry curves (TG-DSC) of salicylaldehyde Schiff bases (BSPs) are presented in Fig.4(a-d). There are endothermic peaks in DSC curves at around 200-225°C in Fig.4(a-c). Because BSP1, BSP2 and BSP3 undergo a phase transition at 200 ° C, 220 ° C, 225 ° C without decomposition, this process has no decomposed weight loss platform in the TG curve. However, the pronounced loss of weight can be observed at 370-390°C in Fig.4(a-c), which were due to that BSP(1-3) decomposed at certain temperature condition. Correspondingly, a remarkable endothermic peak in DSC curve is observed at 370-390°C in Fig.4(a-c). It can be seen that TG-DSC curve of BSP4 was different from BSP(1-3), which had only one exothermic peak in DSC curves and weight loss platform of decomposition in the TG curves at 365°C in Fig.4(d). Moreover, no other phase transitions occurred before the BSP4 decomposition. In addition, the heat change generated by the thermochromic process of BSPs was much smaller than the heat change produced by the phase transition of BSPs, so the thermochromism of BSPs was not reflected as shown in Fig.4(a-d). Therefore, it indicates that BSPs have

poor thermal stability above 360° C.

#### 3.5 Scanning electron microscopy (SEM)

In order to investigate the micromorphology of BSPs, the SEM images have been taken on the surface of the products and are shown in the Fig.5. It can be observed that the BSP1 has a flaky morphology, and the surface is smooth in Fig.5(a). In Fig.5(b), the BSP2 presents rods and blocks morphology with different sizes, and the surface is rough. The both flaky and lump shapes have been observed in Fig. 5(c) for the BSP3. As shown in Fig.5(d), the BSP4 presents the regular and long strip-like morphology and the surface is smooth and regular. The morphology and size of the four products are very different.

## 3.6 Thermochromism and Theoretical study

#### 3.6.1 Thermochromism

The optical images of salicylaldehyde Schiff base (BSPs) are shown in the Fig.6(a-d). The Fig.6(a-d) present that the BSPs have the ability as a reversible thermochromic material. The colors and temperatures of BSPs' reversible thermochromic are shown in Table 2. It can be seen that the salicylaldehyde Schiff base samples have different colors in Fig.6(a-d). At room temperature, the BSP1, BSP2, BSP3 and BSP4 are light orange, orange, lemon yellow and dark yellow, respectively. According to results in section 3.3, the yellowness of the BSPs' color tends to decrease as well (BSP3>BSP1>BSP4>BSP2). During the heating process to the temperature of 145-155 °C, the color of BSP1-3 changed from light orange to red, orange turned into deep orange, and the lemon yellow became orange, respectively.

and the performance was restored after cooling to the room temperature. BSP4 changed color from dark yellow to light orange with heating at  $180^{\circ}$ C, and the color of BSP4 recovered after cooling to room temperature as well. Therefore, the processes of BSPs color changing have been proved to be the reversible thermochromism. Combined with Table 2, BSP1-4 only have differences in color and discoloration temperature, and the processes of color changing are similar, which are reversible thermochromism. Moreover, the color changing of BSP3 was the largest compared with the original color when heating, followed by the BSP1, BSP4 and BSP2. Therefore, with the increasing of the sample light, the  $\Delta$ E1 was increased.

#### 3.6.2 Theoretical study

In order to explore the relationship between thermochromism and structure of samples, four kinds of Salicylaldehyde Schiff base (BSPs) samples were subjected to variable temperature infrared test to observe whether the structure of Schiff base changed under different discoloration temperature. The results are shown in Fig.7.

Fig.7 (a-d) is the infrared spectra of four salicylaldehyde Schiff bases BSP1, BSP2, BSP3, and BSP4 at different temperatures. It can be seen that the molecule structures of BSPs at the discoloration temperature are different from the structures at room temperature. The shifts of the hydroxyl peak were obvious at different the discoloration temperatures, which were disappeared in different salicylaldehyde Schiff bases. And the hydroxyl peak reappeared around at 3400-3500cm<sup>-1</sup> after the cooling. This phenomenon is caused by the proton of hydroxyl group transferring to the nitrogen of imine when heating and called proton transfer.

According to the previous study, the Thermochromism mechanism of salicylaldehyde Schiff bases is related to the molecule structure during heating<sup>[31]</sup>. Under the excitation of heat energy, the hydroxyl proton of salicylaldehyde Schiff bases transfers to the imine nitrogen, and then the enol structure is converted to a ketone structure in Fig.8. Therefore, the absorption spectrum of the molecule changes and the color changes. When cooled, the ketone structure is restored to enol structure and the color is reversible, so the whole process is reversible thermochromism<sup>[25-26]</sup>.

The results of variable temperature infrared spectroscopy support the proton transfer hypothesis that salicylaldehyde Schiff base. Therefore, the thermochromic mechanism of BSP1-4 is a classical proton transfer mechanism.

In order to further understand the thermochromic mechanism of BSP samples, the molecular modeling was carried out using the density functional theory with B3LYP using 6-31G basic sets implemented in a Gaussian 05 program. Fig. 9 gives the optimal geometric configuration of the BSP 1 sample (lactone type) and its cationic BSP' along with the calculated electron distribution in the frontier molecular orbitals (MOS). In BSP1, the HOMO and LOMO are uniformly distributed throughout the entire conjugated molecule. While in the case of BSP', the HOMO was retained on the phenyl ring unit, and the LUMO was localized on the Keto salicylaldehyde structure unit. Fig. 10 shows the energy of the MOs and the energy are corresponding to electron transfer transition ( $\Delta$  E=Homo-LUMO) in BSP1 sample. The results indicate that the  $\Delta$ E value of BSP' is considerably smaller than  $\Delta$ E of the BSP, which is in good agreement with the color from yellow to red and the red shift in the absorption

spectra when BSP1is heated.

#### 3.7 Reversible thermochromic properties

To better measure the thermochromic properties of samples, it can quantify the thermochromism properties of BSPs as two indicators (cycle stability and response time). The Fig.11(a-d) show a visible spectrum of original samples and the samples at room temperature after heating-cooling cycle 50 times. It is obvious that the higher the coincidence degree of the two curves, the better the reduction of the color after cooling to the original color, and the better the cycle stability of the sample. It can be seen that the coincidence of the two curves was high in Fig.11(a) and Fig.11(d), indicating that the color of the sample at room temperature after heating-cooling cycle 50 times is basically same as the color of the original sample. There is a large difference between the two curves in Fig.11(c), and the cycle stability of BSP3 is the worst. Fig.11(f) shows the color difference of BSPs between the color at room temperature after heating-cooling cycle 50 times and original color of the four samples. It can be seen that the color of the BSP1 at room temperature after repeated heating was similar to the original color, followed by BSP2, BSP4 and BSP3.

Fig.11 (e) shows a comparison of the heating discoloration response time and the cooling discoloration response time of the BSPs. Whether it was the heating discoloration or the cooling discoloration response time, the response time of the BSP1 was the shortest, and the response time of BSP3 was the longest. Under the same thermochromic mechanism, the response time of BSPs was different, and it can be considered that this difference comes from the microscopic appearance of BSPs.

Combined with the morphological analysis of the section 3.5, BSP1, BSP2 and BSP4 showed regular shape distribution, and BSP3 had stripes and flakes. Because of its irregular microstructure, the response time of BSP3 was longer than that of other samples when heated or cooled. Besides, the BSPs had a longer cooling discoloration response time than heating discoloration response time. There was a hysteresis<sup>[32]</sup> when the cooling color recovered, and the hysteresis may be related to the energy of BSPs in the discoloration process. Combined with Fig.10, when the energy (heat) was given, the molecule changed from a higher energy level structure to a lower energy level structure, and protons transfer under energy excitation. Conversely, when the energy was disappeared, the proton need spontaneously transfer from the N to O atom and the spontaneous transfer of proton is a slow process. Therefore, the comprehensive cycle stability and response time of sample, the BSP1, BSP2 and BSP4 possessed good the thermochromic performance.

#### 4. Conclusions

In this work, we successfully synthesized four kinds of salicylaldehyde Schiff Base (BSPs) via the solution method and confirm the composition of these target products by HNMR and IR results. It is demonstrated by UV-Vis spectra that the absorption wavelength can be controlled by the type and location of the substituent of BSPs through the variation of the transition mode of the electron, leading to the different colors of samples. With the increase of light colored samples, the content of the  $\Delta$ E1 increases until the maximum value of 48.6. Simultaneously, the thermochromic mechanism of BSPs is mainly contributed by the proton transfer, which is strongly

supported by the *in-situ* IR and DFT calculations. The reversible thermochromic properties are mainly depended on the cycling stability and response time. The higher coincidence degree of two visible spectrum curves after cycles, the smaller  $\Delta E2$  and the better cycle stability of samples. Among all of BSPs, BSP1 owns the best performance, including the smallest  $\Delta E2$  (2.6), the best cycle stability and the shortest response time (10s). Therefore, BSPs can be expected to work as new basic skeletons to combine with different substituents, thus producing promising compounds for the new thermochromism materials.

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#### **Figure captions:**

Fig. 1 Structural representation of the salicylaldehyde Schiff bases BSPs.

Fig. 2 IR spectroscopy of the salicylaldehyde Schiff bases BSPs.

**Fig. 3** (a) UV-visible absorption spectra of BSPs in DMF solvent; (b) UV-visible absorption spectra of BSPs on solid BaSO<sub>4</sub>.

Fig. 4 TG-DSC results of BSPs.

Fig. 5 SEM images of the BSPs: (a) BSP1;(b) BSP2; (c) BSP33; (d) BSP4.

**Fig.6** The reversible thermochromic properties of BSPs from room temperature to discoloration temperature and back to room temperature: (a) BSP1; (b) BSP2; (c) BSP3; (d) BSP4.

Fig. 7 Variable temperatures IR spectra of BSPs: (a) BSP1; (b) BSP2; (c) BSP3; (d) BSP4.

Fig.8 Mechanism diagram of salicylaldehyde Schiff bases' reversible thermochromism.

Fig. 9 Optimized geometry of BSP1 and BSP1'.

Fig. 10 HOMO-LUMO orbitals of the BSP and BSP1' and their energy level diagram.

Fig.11 (a-d): the visible spectrums of original BSPs and the BSPs at room temperature after heating-cooling cycle 50 times. (e): the heating discoloration response time and the cooling discoloration response time of the BSPs. (f): the chromatic aberration( $\triangle E2$ ) of BSPs between the color at room temperature after heating-cooling cycle 50 times and original color.



BSP1: X=H, Y=H, Z=H; BSP2: X=OCH<sub>3</sub>,Y=H, Z=H; BSP3: X=H, Y=OCH<sub>3</sub>, Z=H; BSP4: X=H, Y=H, Z=NO<sub>2</sub>.





Figure 2



Figure 4



Figure 5











Figure 6







Figure 11

## **Table caption**

- Table 11HNMR analysis of BSPS.
- **Table 2**The colors and temperatures of BSPs thermochromic.

### Table 1

Product	1HNMR signals/ ppm <sup>a</sup>					<u> </u>		
	H-3	H-4	Н-5	Н-6	H-7	H-8, H-9	H-a	H-b
С3-Н,С4-Н,С5-Н	7.05(d,2H)	7.40(d,2H)	6.94(t,2H)	7.43(d,2H)	8.67(s,2H)	7.37(s,4H)	13.20(s,2H)	-
СЗ-ОСНЗ	-	7.01(d,2H)	6.91(t,2H)	7.04(d,2H)	8.68(s,2H)	7.38(s,4H)	13.61(s,2H)	3.95(s,6H)
C4-OCH3	6.50(s,2H)	-	6.52(s,2H)	7.28(d,2H)	8.57(s,2H)	7.32(s,4H)	13.75(s,2H)	3.86(s,6H)
C5-NO2	7.01(d,2H)	8.05(d,2H)	-	8.45(s,2H)	9.10(s,2H)	7.35(s,4H)	13.29(s,2H)	-

s=singlet; d=duplet; t=triplet; H-a=signal corresponding to H of the OH group; H-b=signal corresponding to H of the MeO group.

<sup>a</sup> For assignments see Fig. 1.

Table 2				
				$\Delta E1$ (Chromatic
Sample	Initial color	The color	Temperature of	aberration between
		after heating	thermochromic /°C	color after heating and
				initial color of sample )
BSP1	Light orange	Red	150	19.5
BSP2	Orange	Dark orange	155	14.6
BSP3	Lemon yellow	Orange	180	48.5
BSP4	Dark yellow	Light orange	145	14.8

## **Research Highlights**

- Four salicylaldehyde Schiff Base substituted with methoxy and nitro groups are synthesized.
- Their novel reversible thermochromic properties are highlighted.
- The sample shows the good cycling stability and rapid response time.
- The samples can be used as a basic skeleton to combine different substituents together to produce promising compounds for the new thermochromic materials.